A COMPARATIVE MUON SPIN RELAXATION (μSR) STUDY OF TITANIUM AND YTTRIUM DIHYDRIDES*

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Summary

Transverse depolarization data have been obtained for positive mu⟨ in powder samples of TiH_x ($x = 1.99$, 1.97 and 1.83) and $YH_{2.00}$. As a fu⟨ tion of temperature all samples show two plateaux in the depolarization ra⟨ The lower temperature plateau for TiH_x is interpreted as indicating t⟨ near $x = 2$ muons mainly occupy octahedral (O) sites, being unable to re⟨ a vacant preferred tetrahedral (T) site on the hydrogen sublattice. ⟨ decrease to the higher temperature plateau is attributed to the escape ⟨ muons from O sites to vacant T sites. The data are consistent with O ⟨ occupation by hydrogen equal to zero. The results for $YH_{2.00}$ are qu⟨ titatively different in that the plateau values indicate predominant T ⟨ occupation by hydrogen but with about 4% of the O sites occupied.

1. Introduction

To understand the microscopic features of the distribution and ⟨ fusion of light interstitial particles in metals, it is desirable to use a var⟨ of techniques which might include neutron scattering, nuclear magr⟨ resonance (NMR) of hydrogen, deuterium and metal nuclei, and μ^+Sl⟨ which one can regard the positive muon as a light isotope of hydrogen.

In this paper we report on μSR experiments on non-stoichiometric titanium and yttrium dihydrides which have similar structures. The metal atoms in each case form an f.c.c. lattice and the hydrogen ions occupy interstitial sites which in $TiH_{\approx 2}$ are known to be the tetrahedral (T) sites (forming a simple cubic lattice with a lattice parameter half that of the metal lattice, see Fig. 1) and in $YH_{\approx 2}$ a similar structure occurs except
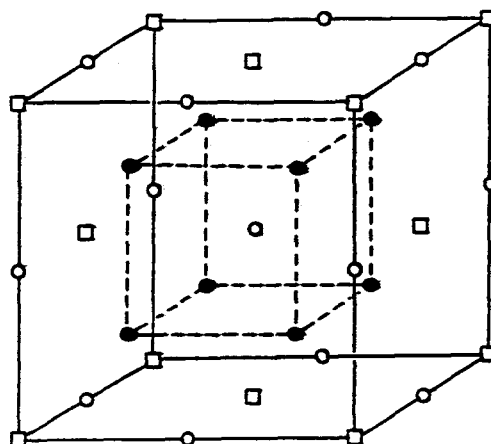

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Fig. 1. The fluorite structure of γ-TiH$_2$ and γ-YH$_2$ phases: □, metal atoms; ●, tetrahedral hydrogen sites; ○, octahedral sites.

that it is believed that a small proportion of the octahedral (O) interstitial sites (forming an f.c.c. lattice identical with the metal lattice) are occupied by hydrogen ions at the expense of a fraction of the preferred T sites [1, 2]. One of the objects of the present experiments was to search for differences between μSR characteristics for the two systems which might reflect and quantify the extent of O site occupation.

The basic experiment proceeds by examining the muon depolarization rate. It is convenient to make these measurements in a modest transverse magnetic field and to observe the time dependence of the muon decay signal produced by the resulting precession. It can also be helpful in investigating the onset of muon diffusional motion to make measurements in zero magnetic field. At low temperatures where the muons and hydrogen nuclei are both stationary, the muon samples the local dipolar fields of the protons (in the present cases the metal nuclei do not contribute appreciably to the dipolar field) and the consequent dephasing rate is a sensitive measure of the dipolar fields and hence of the sites occupied by the muons and, simultaneously, of the disposition of the protons around them. At higher temperatures both muons and protons can diffuse and the observed depolarization rates then reflect the time-average dipolar field (in a manner analogous to motional averaging in NMR) and hence yield information on the diffusional motions of both species.

2. Experimental details

The samples consisted of metal powders hydrided to various γ-phase (f.c.c.) compositions directly from the gas phase. The sample thickness was of the order of 2.5 g cm^{-2} to provide adequate muon stopping power, and samples were contained in evacuated aluminum cells provided with mylar

windows. The purity was such that the chance of trapping of muons by residual impurities could be neglected. Indeed no trapping of muons by point and other defects was anticipated (or found) since such traps would already be saturated by hydrogen ions. The particle size was 75 - 150 μm which was sufficiently large so that no complications owing to diffusion to, and depolarization at, particle surfaces needed to be considered. The samples investigated were of compositions $TiH_{1.99}$, $TiH_{1.97}$, $TiH_{1.83}$ and $YH_{2.00}$.

Magnetic fields of 150 G were provided by Helmholtz coils providing a precession rate in the transverse mode of about 2 MHz. A temperature range $10 \text{ K} < T < 600 \text{ K}$ was attained by use of a helium closed-cycle refrigerator and a conventional furnace. The muon beam and attendant experimental facilities will be described elsewhere [3].

3. Results

The depolarization rates observed in a transverse field were represented for all samples by a function $\exp(-\Lambda^2 t^2)$. At low temperatures at which muon motion does not occur $\exp(-\Lambda^2 t^2) = \exp(-\sigma^2 t^2/2)$ where σ^2 is the second moment of the frequency distribution owing to the dipolar fields [4]. At high temperatures, for the purpose of extracting diffusion information, the more general function

$$\exp\left[-\sigma^2\tau^2\left\{\exp\left(\frac{-t}{\tau}\right) - 1 + \frac{t}{\tau}\right\}\right]$$

was used to take account of random time fluctuations of the dipolar field experienced by the muons, owing to muon and/or proton motions, with correlation time τ [4]. This formula was used to analyse the higher temperature data where a gaussian shape function would not be expected to hold. The experimental results for $\Lambda(T)$ as a function of temperature are shown in Figs. 2 and 3.
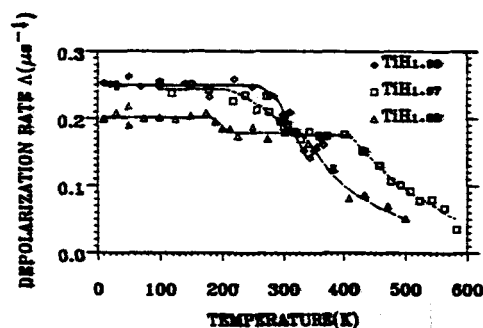

Fig. 2. Depolarization rates for titanium dihydride samples as a function of temperature. The lines are included as a guide to the eye.
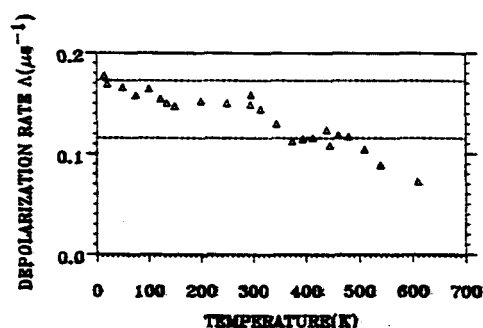
Fig. 3. Depolarization rate for yttrium dihydride as a function of temperature. The upper and lower broken horizontal lines indicate Λ_O and Λ_T respectively.

Zero field measurements were made for $YH_{2.00}$ at 20 K and 295 K. The curve at 20 K shows some recovery of the dephasing function $G(t)$ towards $\frac{1}{3}G(0)$ after passing through a minimum, though without ever reaching the value $\frac{1}{3}G(0)$, which is the asymptotic value for a stationary muon; this is consistent with there being only very slow diffusional motion of the muons at this temperature as indicated by the transverse field data. The curve at 295 K shows no recovery following the initial decay, again confirming that considerable muon motion is occuring ($\sigma\tau < 3$).

4. Discussion

We first discuss the low temperature results for the Ti–H system. As a function of temperature all samples show two plateaux in the depolarization rate Λ followed at high temperatures by a continuous decrease in Λ. Below a sample-dependent temperature, Λ takes a temperature-independent value which increases as the hydrogen concentration increases. This is shown in Fig. 4 where the square of this value of Λ is plotted as a function of fractional vacancy concentration on the T sublattice, $(2-x)/2$. The data can thus be represented by a linear relation. This significant result is interpreted as indicating that at high hydrogen concentrations muons come to rest in O sites and remain there except in those instances where one of the eight nearest neighbor T sites happens to be vacant. Under these circumstances the observed average depolarization rate is a weighted mean:

$$\Lambda_{exp}^{2} = \Lambda_{O}^{2}\left[1 - \left\{\frac{8(2-x)}{2}\right\}\right] + \Lambda_{T}^{2}\left\{\frac{8(2-x)}{2}\right\} \tag{1}$$

where the values Λ_{O} and Λ_{T} are the rates characteristic of O and T sites respectively, arising from the dipolar interactions with surrounding protons. The straight line is calculated from eqn. (1); the value of Λ_{T} for best fit to the data coincides with the higher temperature plateau value common to $TiH_{1.97}$ and $TiH_{1.83}$. The significance of this will be discussed below.
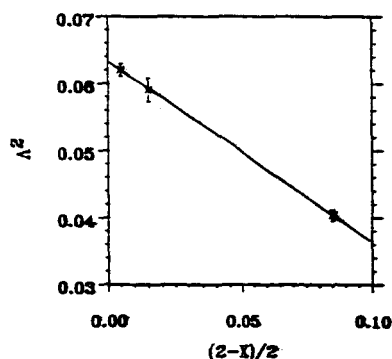

Fig. 4. The low temperature value of Λ^{2} for TiH_{x} samples as a function of vacancy concentration $(2-x)/2$.

In calculating Λ_O and Λ_T [4] it is necessary in principle to allow for the mutual spin-flip rate of the protons which reduces the fourth moment of the muon signal without affecting the second moment. This has the effect of narrowing the observable part of the signal [5] and changing the shape from a gaussian to some extent. We estimate that here the fourth moment is reduced by 23% compared with a situation in which the proton spin orientations are frozen; the deviation of the line shape from gaussian is not large and is indeed undetectable, and the observed linewidth is decreased by approximately 5%. The resulting calculated value of Λ_O is 0.298 μs^{-1} compared with the experimentally fitted value of (0.252 ± 0.004) μs^{-1}. The small difference is plausibly accounted for by a local displacement of nearest neighbor protons away from the muon by 0.1 Å.

Our interpretation of the lower plateaux observed at higher temperature is that here the muon is sufficiently mobile that it is able to locate a vacancy on the T lattice. The new values of Λ_T (0.189 μs^{-1} calculated; (0.172 ± 0.005) μs^{-1} fitted) for TiH_x are consistent with this interpretation if we postulate a small (approximately 0.07 Å) local expansion around the muon, or alternatively take the muon wavefunction to be spread out around the T site, with a small probability density on the four neighboring O sites.

The low temperature results for $YH_{2.00}$ are quantitatively different from that for TiH_x even when allowance is made for the difference in lattice constants. At the lowest temperature, Λ increases to a value appropriate to a situation in which all T sites are filled by protons (there are two T sites per metal atom) and all muons must therefore reside on O sites. The upper horizontal broken line in Fig. 3 represents Λ_O and passes through the low temperature limiting value of the data.

As soon as the temperature begins to increase, however, Λ decreases. This is simply explained if one makes the assumption that a proportion of protons relax from their T sites to nearest O sites; this process does not require that protons should be capable of diffusional motion at this low temperature, of course. The vacated T sites are then available for muon occupation. The plateau value reached shows that, according to eqn. (1), (4.2 ± 1.5)% of O sites are occupied. This result is to be compared with the value obtained from NMR [1] of (15 ± 3)% at 180 K, and that obtained from neutron diffraction [2] of (12 ± 6)% at 11 K and (13 ± 3)% at 300 K. This fraction is not expected to change appreciably with temperature [6] since the effect of the normal Boltzmann factor is thought to be counteracted by large amplitude hydrogen vibrations at high temperature, which inhibit occupation of nearest neighbor T and O sites.

At higher temperatures ($T > 360$ K) when all the muons are capable of searching out vacant T sites, a further small reduction in Λ occurs as expected. The lower horizontal broken line through the value of Λ_T in Fig. 3 is obtained by simple scaling from the TiH_2 case.

The highest temperature decrease in Λ for all samples occurs in the temperature ranges in which motional narrowing of the proton NMR absorption lines takes place [7, 8], and is clearly associated with proton diffusional
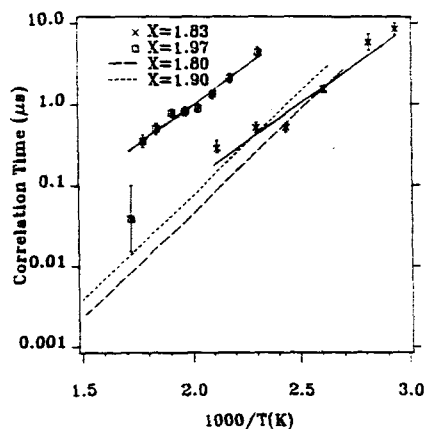
Fig. 5. Diffusional correlation times for muons and protons in TiH_x deduced from the motional decrease of Λ (experimental points) and the NMR motional narrowing (broken lines, from ref. 8) respectively, as a function of reciprocal temperature.

motion. Since the muon can only move when a proton (or a vacancy) moves, one might expect that both τ_O and E_a characterizing the muon motion ($\tau = \tau_O \exp(E_a/kT)$) would be identical with that deduced for protons from NMR relaxation data. Although the absolute values of τ for TiH_x (see Fig. 5) are indeed similar for muons and protons, the values of E_a are quite distinctly smaller for muons than protons; 0.38 ± 0.02 eV for TiH_x for muons compared with 0.505 eV for protons [8]. For $YH_{2.00}$ we obtain 0.4 ± 0.1 eV for muons compared with 0.435 eV for protons [9]; the uncertainty is large enough that it is not clear whether a real difference exists for $YH_{2.00}$. We believe that the results for TiH_x indicate significant muon–proton interactions as discussed for NbH_x by Richter *et al.* [10]. A detailed discussion of this point will be presented elsewhere [11].

5. Conclusion

There is a significant difference in site occupation by hydrogen in γ-TiH_x and γ-YH_x. In the former the hydrogen occupies solely tetrahedral sites, whereas in the latter at $x = 2.0$ approximately 4% of hydrogen ions occupy octahedral sites, except at the lowest temperatures ($T < 50$ K).

The activation energy for muon diffusion for the Ti–H system is considerably lower than that deduced for protons from NMR studies. This is attributed to muon–proton interactions. Similar considerations may apply to $YH_{2.00}$, but a firm conclusion must await the results of measurements at higher temperatures for this system, which are currently in progress.

Acknowledgments

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